High performance anode based on a partially fluorinated sulfonated polyether for direct methanol fuel cells operating at 130 °C

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HIGHLIGHTS

- Partly fluorinated sulfonated polyether was used as ionomer in a DMFC anode at 130 °C.
- The activity for the methanol oxidation is comparable with Nafion based anodes.
- Degradation is reduced due to the high thermal and chemical stability of the polymer.
- The anode has a high mechanical stability and adhesion on the Nafion membrane.
- MEA operation at ambient cathode pressure is possible with high performance.

ARTICLE INFO

ABSTRACT

Due to the disadvantages of the Nafion polymer for the application in the direct methanol fuel cell (DMFC) especial at temperatures above 100 °C several polymers of the hydrocarbon type have already been investigated as membranes and ionomers in the DMFC. Among them were nonfluorinated and partially fluorinated arylene main-chain hydrocarbon polymers. In previous work, sulfonated polysulfone (sPSU) has been applied as the proton-conductive binder in the anode of a DMFC, ending up in good and stable performance. In continuation of this work, in the study presented here a polymer was prepared by polycondensation of decafluorobiphenyl and bisphenol AF. The formed polymer was sulfonated after polycondensation by oleum and the obtained partially fluorinated sulfonated polyether (SFS) was used as the binder and proton conductor in a DMFC anode operating at a temperature of 130 °C. The SFS based anode with 5% as ionomer showed comparable performance for the methanol oxidation to Nafion based anodes and significant reduced performance degradation versus Nafion and sPSU based anodes on the Nafion 115 membrane. Membrane electrode assemblies (MEAs) with the SFS based anode showed drastically improved performance compared to MEAs with Nafion based anodes during operation with lower air pressure at the cathode.

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1. Introduction

In previous studies of the involved and other working groups, different nonfluorinated [1—4] and partially fluorinated [5—7] hydrocarbon polymer proton conductors based onto arylene main-chain polymers such as polybenzimidazole (PBI) doped with phosphoric acid [8,9] have been investigated as the membrane in DMFCs. The investigated membranes showed good to excellent DMFC performance in the temperature range from 25 °C to 200 °C which is due to their lower methanol permeability, compared to Nafion as the membrane material [10]. In the MEAs assembled using this membrane, Nafion was however used as the polymeric and proton-conductive binder in the electrode. This led to a limitation of contact between the three-phase interlayer and the membrane and therefore to a limitation of DMFC performance [3,11]. It can be comparable to the performance of MEAs containing Nafion in both the electrode and the membrane respectively, but the methanol permeability of the hydrocarbon membranes is usually significantly lower than that of Nafion. The origin of limitation of DMFC performance is insufficient contact between the electrodes and the membrane, leading to insufficient utilization of

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the three-phase interlayer, because of the dissimilarity of the chemical nature of hydrocarbon membrane and PFSA (perfluorosulfonic acid, Nafion-type) ionomer in the electrode; this leads to incompatibility between the electrode ionomer and the membrane polymer, respectively, due to hindrance of charge transport between the polymer particles in the electrode and in the membrane.

The ionomer strongly influences the properties of the electrodes, e.g. proton resistance [12]; therefore various sulfonated polymers [13] such as sulfonated polysulfone [14] were investigated as alternative to Nafion. However, low proton conductivity [15], decreased electrode pore size [16] and insufficient chemical and thermal stability of these ionomers [17] decrease the cell performance compared to MEAs based on Nafion electrodes [18–20].

In this study, anodes have been built up using the partially fluorinated polymer SFS (Fig. 1) which is made by polycondensation of decafluorobiphenyl and 6F bisphenol, followed by sulphonation of the highly fluorinated arylene main-chain polymer. The synthesis of the polymer is shown in Fig. 1.

The optimization of synthesis of this ionomer was described in a previous article [21]. It could be shown that the ionomer holds outstanding thermal and chemical stabilities.

2. Experimental

The synthesis of SFS and the optimization procedure are described in Ref. [21] and in Ref. [22]. The same commercial available materials were used as in Ref. [14].

2.1. Preparation of the ionomer solutions and catalyst ink

The SFS solution was prepared by its dissolving in an aqueous 40 wt% isopropanol solution via an ultrasonic bath. Subsequently
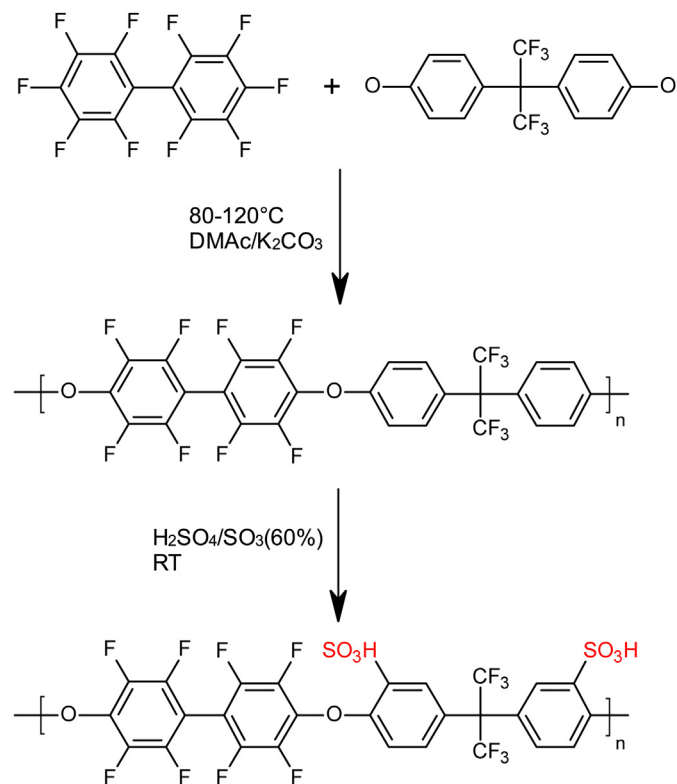

Fig. 1. Preparation of the SFS ionomer.

the isopropanol was removed by evaporation and replaced by water to receive an aqueous safe SFS solution. For the anode inks, 0.5 g PtRu black (Johnson Matthey HISPEC 6000) was dispersed in 5 g millipore water. Subsequently, the ionomer solutions were added. The cathode was prepared from 40% Pt/C (Heraeus). The Nafion containing inks were stirred magnetically for at least 3 days, the inks with SFS at least 6 h.

2.2. MEA preparation

Nafion 115 membranes were conditioned by boiling in 3% H_2O_2 in order to remove organic contaminants followed by successive boiling in millipore water, 0.5 M sulphuric acid and a second time in millipore water each time for 1 h.

Wet Nafion 115 membranes were fixed in an aluminium frame covered by a polymer foil and dried at 80 °C in an oven. The catalytic layers were prepared by spraying of the catalyst inks in multiple layers directly onto the polymer electrolyte membrane at a substrate temperature of 100 °C. The catalyst loading was determined by weighing the dried MEA. The anode loading was defined as 3 mg cm^{-2} PtRu, the cathode loading as 1 mg cm^{-2} Pt.

2.3. Electrochemical characterization

The single cell setup, the test station and the electrical devices are described in Ref. [14]. Half-cell and full cell configurations have been used. In the half cell setup the anode was fed with 1 M methanol solution at a flow rate of 6 mL min^{-1}. The cathode was fed with 50 mL min^{-1} hydrogen at atmospheric pressure to make a reversible hydrogen electrode (RHE). In the full cell setup the anode was fed with 1 M methanol solution while the cathode was fed with air. Methanol crossover was measured by CO_2 release from the cathode.

Methanol adsorption on the PtRu anode catalyst was studied by methanol stripping cyclic voltammetry (CV). Before starting the methanol stripping the cell was flushed with deionised water and CVs were performed from 0 to 800 mV vs. RHE until the result was stable. The peak in the range of the methanol oxidation served as baseline for the determination of the methanol oxidation peaks. Subsequently, methanol was adsorbed at a potential of 0 V vs. RHE from 1 M aqueous methanol solution during 5 min followed by flushing the cell with deionised water for 30 min. Three cycles were recorded with a scan rate of 10 mV s^{-1} by cycling the electrode potential from 0 to 800 mV at a cell temperature of 130 °C. The active anode area was calculated from the first peak and all potentials were IR-corrected.

Voltage−current curves were measured galvanostatically at 130 °C with 2.8 bar anode pressure and 4 bar cathode pressure absolutely. The current was held for 2 min before the voltage was recorded. For this measurement the cell with an active area of 25 cm^2 was used. The stoichiometry factor for methanol was fixed at $\lambda = 2$ and for air at $\lambda = 4$. Before the measurement, the cell was conditioned potentiostatic at cell voltage 0.4 V and at $T = 130$ °C about 8−10 h. Polarization curves were measured in the half-cell setup by manually electrode potential variation in the potential range between resting potential and 500 mV.

2.4. Physical characterization

The water uptake of the ionomer and its release over time at room temperature was determined by measuring the weight loss of fully hydrated Nafion 115, sPSU and SFS membranes. Surface and cross-sectional morphologies of the anodes and MEAs were investigated with scanning electron microscopy (Zeiss LEO 1530
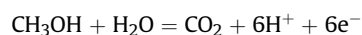
VP). The MEA cross-sections were made by submerging the MEAs in liquid nitrogen and then fracturing.

3. Results and discussion

3.1. Ionomer's water absorption and its release over time

Water absorption and its release over time of SFS, sPSU and Nafion at room temperature are compared in Fig. 2. Nafion shows the slightest water absorption with about 25% which is less than half of the sPSU water absorption capacity; SFS even has a water capacity of a factor 9 higher versus the Nafion 115 membrane. SPSU and Nafion release the water quite fast, after 10 min most of the saved water is evaporated. However structurally bonded water can not be observed by this method. The water release from SFS is steady over a long time and lasts over an hour. Stabilisation of the polymeric backbone by fluorination ensures the stability of the SFS polymer with two SO_3H groups per repeat unit which is twice as high as for sPSU. Conductivity and water uptake of the polymers are usually increased at high sulphonation degrees.

Slow water release from the ionomer provides a more stable water support for the three-phase interlayer. High water absorption buffers variations in the water and methanol support especially during CO_2 evolution at the methanol oxidation reaction (MOR):

$$CH_3OH + H_2O = CO_2 + 6H^+ + 6e^-$$

3.2. Electrochemical half cell investigations of the SFS based anodes

The active area for the methanol oxidation of anodes with different binders was determined by methanol stripping experiments [23]. The ionomer content in the electrodes supports the formation of the three-phase interlayer. Ionomers are acting as a buffer and a barrier for methanol and water. To quantify the anode active area, the charge of the methanol oxidation was measured. Anodes with different ionomers are compared in Fig. 3.

The methanol oxidation charge of the 5% SFS bonded anode is between the values for the anodes with 15% Nafion and 5% sPSU. Blocking of the catalyst by ionomer is reduced compared to the Nafion anode by reduced ionomer content in the anode. More adsorption sites in the catalyst layer improve potentially the kinetics of the methanol oxidation, especially at high current
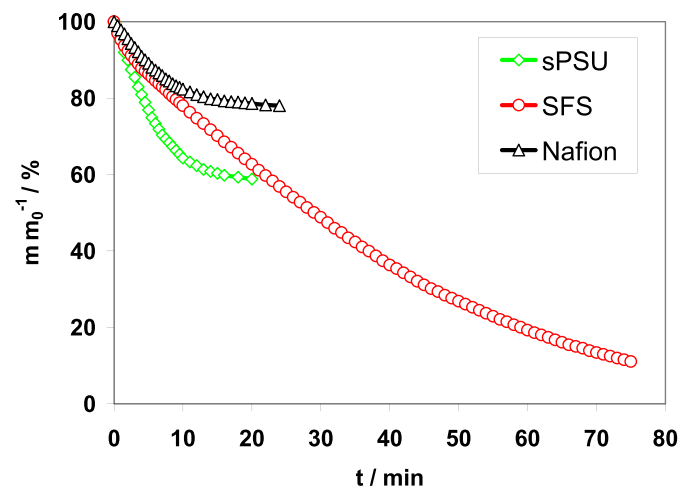

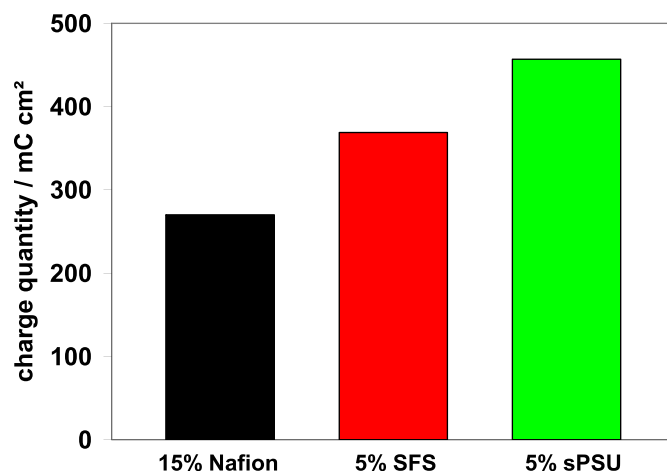**Fig. 3.** Charge quantity of the methanol oxidation. $A = 25$ cm^2, anode: $T = 130$ °C, 1 M MeOH, 4 mL min^{-1}, $p_a = 2.8$ bar, half cell setup.

densities. However more significant for the MOR is not quantity but quality of the three-phase interlayer, where the ionomer properties play an important role.

Fig. 4 shows a comparison of the polarization curves for methanol oxidation at a temperature of 130 °C for different anode ionomers. Activity for anodes based on SFS or Nafion is comparable and higher than for anodes bonded with sPSU. At high current densities the SFS and sPSU based anodes show mass or charge transport hindrances, which can not be explained here.

The long-term stability of the anodes was measured galvanostatically in a half cell setup (Fig. 5). The performance degradation of the anode based on 5% SFS is significantly smaller compared to the anode based on 5% sPSU and the 15% Nafion bonded anode. However the general behaviour of the performance degradation of the anodes with the time is similar. The performance loss of the three anodes is reversible. After a few minutes of operation at open circuit voltage, the initial anode potential level is usually reached again.

The outstanding chemical and thermal stability of SFS reduces the degradation of the SFS bonded anode; the ionomer is not diluted in hot methanol solutions like Nafion [24]. Constant supply with methanol and water (compare Fig. 2) enables long-term high
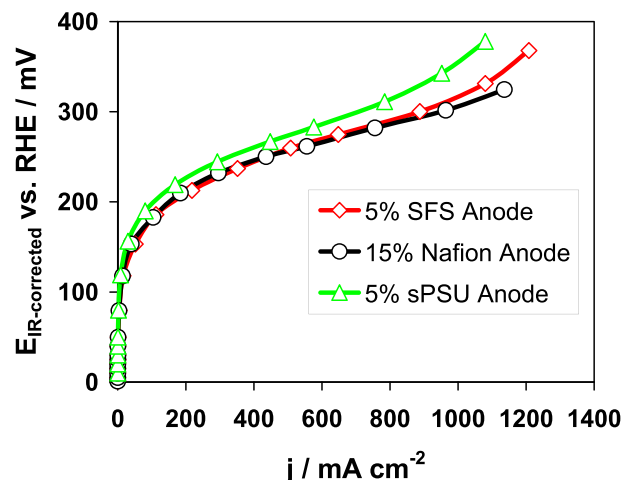

Fig. 2. Water adsorption and its release over time of SFS, sPSU and Nafion. $T = 25$ °C.

Fig. 4. Activity of anodes bonded with SFS, sPSU or Nafion. $T = 130$ °C, $A = 25$ cm^2, Nafion 115 membrane, anode: 1 M MeOH, 4 mL min^{-1}, $p_a = 2.8$ bar, half cell setup.
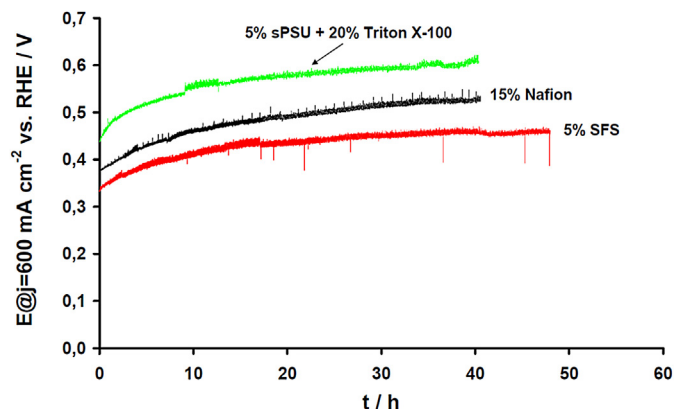
Fig. 5. Long-term stability of anodes with SFS, sPSU or Nafion as ionomer. $T = 130\,°C$, Nafion 115 membrane, $A = 25\,cm^2$, 3 mg PtRu cm^{-2}, GDL: SGL 10BB, $\lambda_{1M\ MeOH} = 2$, $p_a = 2.8$ bar, half cell setup.

Fig. 7. Methanol crossover of MEAs with a SFS or a Nafion bonded anode. $T = 130\,°C$, Nafion 115 membrane, $A = 25\,cm^2$, anode: 3 mg PtRu cm^{-2}, GDL: SGL 10BB, $p_a = 2.8$ bar, $\lambda_{1M\ MeOH} = 2$; cathode: 1 mg Pt cm^{-2}, GDL: SGL 10BB, $p_c = 4$ bar, $\lambda_{air} = 8$.

activity and retards reversible degradation of the SFS bonded anode.

3.3. DMFC full cell investigations

The performance of the MEA based on the 5 wt% SFS anode strongly depends on the air stoichiometry factor λ (Fig. 6), which was also observed for sPSU bonded anodes (compare [14]). At a stoichiometry λ (air) = 8 the MEA with the SFS based anode achieves a comparable performance to MEAs with Nafion based anodes. However λ (air) = 8 is not suitable for practical operation. The SFS anode does not sufficient work as a barrier; therefore the cathode is partially flooded with water. High air stoichiometry is necessary to remove additional water. The cathode needs to be adapted to the new anode or a barrier layer at the cathode must be setup.

Methanol crossover for MEAs based on a 5% SFS respectively 15% Nafion anode is comparable at small current densities (Fig. 7); it is significant reduced versus MEAs with a sPSU based anode with 20% Triton X-100 [14]. This indicates the MeOH crossover limitation is mainly caused by the Nafion 115 membrane and not by the SFS based anode. Until 200 mA cm^{-2} methanol and air are supplied at
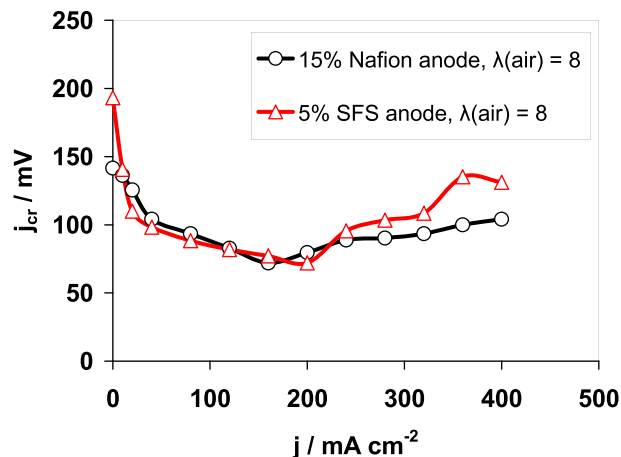
constant flow. The methanol crossover decreases in this area due to the decreased methanol gradient between anode and cathode by higher methanol consumption on the anode. At current densities above 200 mA cm^{-2} the methanol and air supply is stoichiometric. The methanol crossover of the MEA with the Nafion based anode slightly increases while it distinctly increases at 350 mA cm^{-2} for the MEA with the SFS based anode. These differences can not be explained in the frames of the submitted work.

The performance of the 5% SFS anode was also investigated with MEAs based on a hydrocarbon membrane made from the polymer SFS-F$_6$PBI [25] as shown in Fig. 8. The performance is comparable with MEAs based on a 5% SFS anode and a Nafion 115 membrane. A peak power density of 230 mW cm^{-2} is achieved which is quite high compared to MEAs based on other hydrocarbon polymers in the field of medium temperature DMFCs [2,19] such as sulfonated polyether ether ketone (sPEEK) [26], sulfonated polysulfone [27] or sPEEK modified with zirconium phosphate and PBI [28].

In previous work was shown, that the anode properties can affect strongly the cell performance at reduced cathode pressure [14]. The cathode pressure dependence of the cell voltage over time behaviour of MEAs with Nafion based anodes is shown in Fig. 9. The
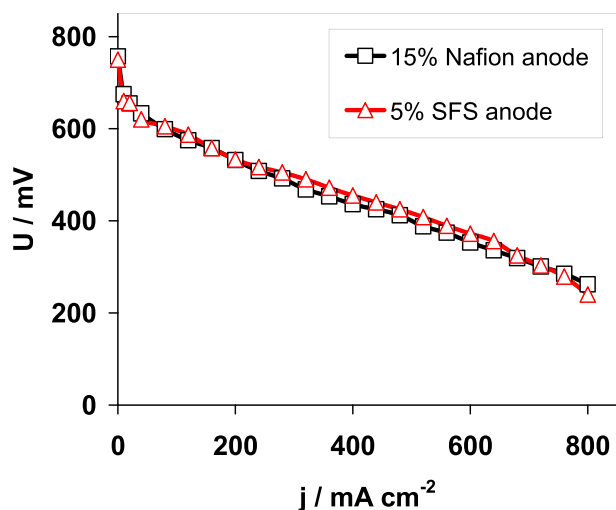

Fig. 6. Performance of MEAs with a SFS or a Nafion bonded anode. $T = 130\,°C$, Nafion 115 membrane, $A = 25\,cm^2$, anode: 3 mg PtRu cm^{-2}, GDL: SGL 10BB, $\lambda_{1M\ MeOH} = 2$, $p_a = 2.8$ bar; cathode: 1 mg Pt cm^{-2}, GDL: SGL 10BB, $p_c = 4$ bar, $\lambda_{air} = 8$.
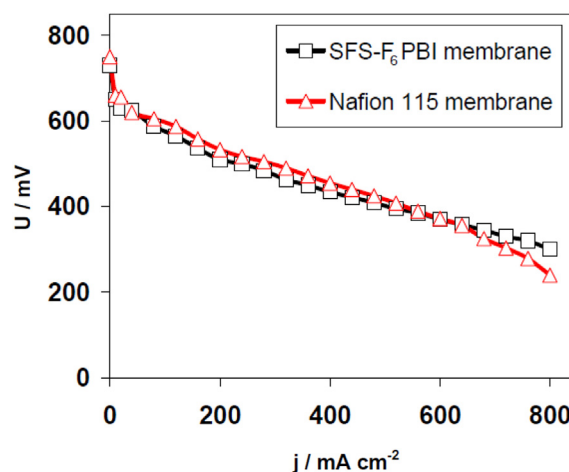

Fig. 8. Performance of MEAs with a SFS bonded anode and a SFS-F$_6$PBI or a Nafion membrane. $T = 130\,°C$, $A = 25\,cm^2$, anode: 3 mg PtRu cm^{-2}, GDL: SGL 10BB, $\lambda_{1M\ MeOH} = 2$, $p_a = 2.8$ bar; cathode: 1 mg Pt cm^{-2}, GDL: SGL 10BB, $p_c = 4$ bar, $\lambda_{air} = 4–6$.

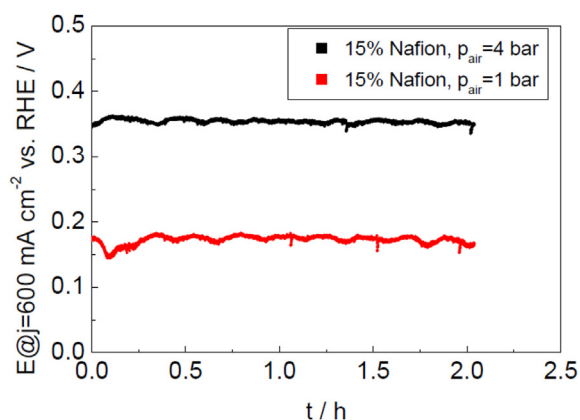**Fig. 9.** Performance of a MEA based on a 15% Nafion anode at reduced air pressure. Nafion 115 membrane, $T = 130\,^\circ C$, $A = 25\ cm^2$, anode: 3 mg PtRu cm^{-2}, GDL: SGL 10BB, $p_a = 2.8$ bar, $\lambda_{1M\ MeOH} = 2$; cathode: 1 mg Pt cm^{-2}, GDL: SGL 10BB, $p_k = $ var., $\lambda_{air} = 10$, $j = 600$ mA cm^{-2}.
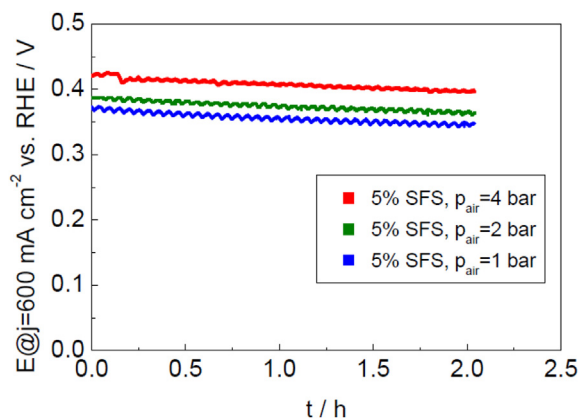

Fig. 10. Performance of a MEA based on a 5% SFS anode at reduced air pressure. $T = 130\,^\circ C$, Nafion 115 membrane, $A = 25\ cm^2$, anode: 3 mg PtRu cm^{-2}, GDL: SGL 10BB, $p_a = 2.8$ bar, $\lambda_{1M\ MeOH} = 2$; cathode: 1 mg Pt cm^{-2}, GDL: SGL 10BB, $p_k = $ var., $\lambda_{air} = 10$, $j = 600$ mA cm^{-2}.

voltage loss at 600 mA cm^{-2} is about 50% at 1 bar air pressure at the cathode compared to 4 bar air pressure and not suitable for high performance applications. Dehydration of the Nafion ionomer in the cathode at low air pressure is suspected to cause the voltage

loss. Although a high air stoichiometry ($\lambda = 10$) is necessary for the cell operation due to too complicated water management at the cathode. However it can be reduced with an adapted cathode design.

The influence of the cathode pressure on the voltage over time behaviour of MEAs with SFS based anodes is significantly lower than for MEAs with Nafion bonded anodes (Fig. 10). The voltage loss compared to operation with 4 bar air pressure is only about 10–15% at operation with 2 respectively 1 bar absolute air pressure. The voltage decay rate is similar for both cases.

The SFS bonded anodes are a weaker barrier for water than Nafion based anodes, therefore the water transport through the membrane is increased and dehydration of the cathode at 130 $^\circ C$ is avoided. It is evident that at lower cathode pressure, cell voltage is only slightly lower for MEAs with SFS based anodes. From a system's point of view, operation at lower pressure is favourable since energy consuming air compression and system size can be minimized.

3.4. Morphology of the anodes

The SFS bonded anode has a homogenous and very dense structure compared to the Nafion bonded anode with quite tall agglomerates on its surface (Fig. 11). The Nafion bonded anode has a more distributed pore structure with greater pores due to the agglomerates inside the anode.

The adhesion between the SFS bonded anode and the Nafion 115 membrane is very good due to the similar (hydrophobic) properties of the ionomer SFS and the Nafion membrane (Fig. 12). Therefore, a high cell performance is achieved compared to MEAs with Nafion bonded electrodes and hydrocarbon polymer membranes [11]. Cracks in the catalyst layer are caused probably by the extreme dehydration of SFS under the ultra high vacuum conditions in the scanning electron microscope (SEM). At normal operation conditions the SFS bonded anode is stable. As expected, the adhesion between the Nafion based anode and the Nafion membrane is also very good. The anodes have similar thickness.

The SFS bonded anode shows a homogenous distribution of platinum and fluorine, which is contained in SFS; however there are some SFS agglomerates in the anode (Fig. 13). The distribution of platinum and fluorine in the Nafion bonded anode is less homogenous. Therefore the active area in the Nafion bonded anode is reduced by the high number of inactive agglomerates (comp. Fig. 3).
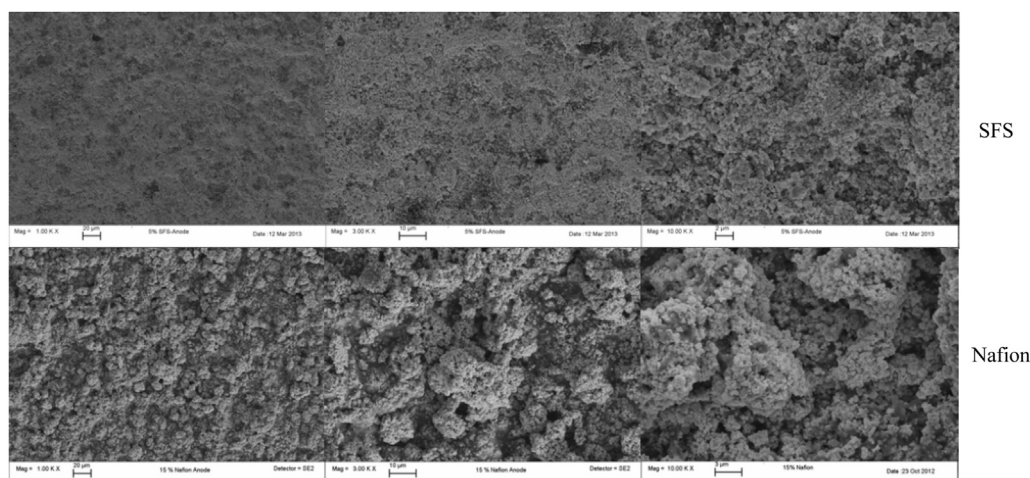

SFS

Nafion

Fig. 11. SEM-images of the surface of SFS and Nafion bonded anodes. Magnification: 1000× (left), 3000× (middle), 10,000 (right); up: SFS bonded anode, down: Nafion bonded anode.
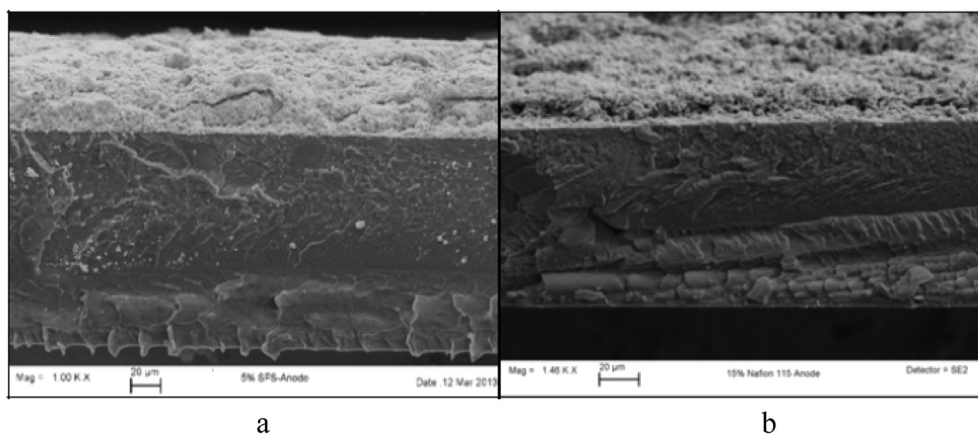
Fig. 12. SEM-images of the cross-section of SFS and Nafion bonded anodes. Magnification: 1000×; left: SFS bonded anode, right: Nafion bonded anode, Nafion 115 membrane.
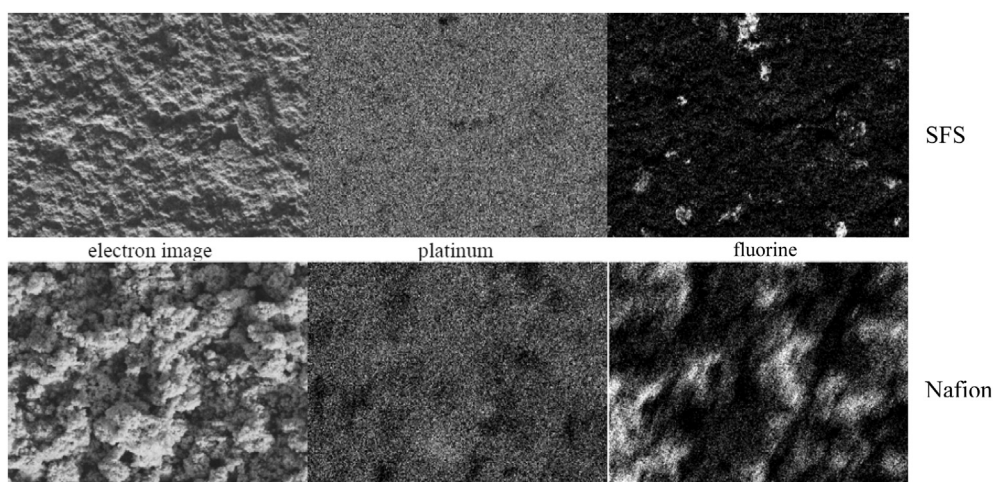

Fig. 13. Mapping (energy dispersive X-ray spectroscopy, EDX) of SFS and Nafion bonded anodes; up: SFS bonded anode, down: Nafion bonded anode.

4. Summary and conclusions

In this work, the SFS polymer was investigated as an ionomer in the anode catalyst layer of a medium temperature DMFC. The activity for the methanol oxidation of the novel anode with 5% SFS is comparable to anodes with 15% Nafion content. The cell performance degradation is reduced due to the high thermal and chemical stability of SFS and constant supply of the three-phase interlayer with methanol and water. Methanol crossover of MEAs based on the SFS anode is comparable to Nafion based MEAs.

The mechanical stability and adhesion of the new anodes on the Nafion membrane are good at the operating conditions of DMFCs using an operating temperature of 130 °C. The active area for the methanol oxidation is high because of the homogeneous distribution of catalyst and SFS in the anode. MEA operation at ambient air pressure is possible due to improved hydration of the cathode by increased water transport through the membrane.

In this work it was shown, that the partially fluorinated sulfonated polyether SFS is a promising alternative for Nafion as conductive binder in a DMFC anode catalyst layer. However further optimisation of MEAs based on the novel anode is necessary, especially a suitable cathode has to be developed to reduce the air stoichiometry at the cathode. Further work will be dedicated to study SFS- and sPSU-based electrodes applied to hydrocarbon membranes for DMFC operation.

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